Metal-insulator transition in amorphous alloys

A. Möbius[1] and C.J. Adkins[2]

[1]*Institute for Solid State and Materials Research Dresden, D-01171 Dresden, Germany, e-mail: a.moebius@ifw-dresden.de,*

[2]*Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK, e-mail: cja13@cam.ac.uk*

Abstract

We focus on the central problem of discriminating between metallic and insulating behaviour in amorphous alloys formed between a semiconductor and a metal. For this, the logarithmic temperature derivative of the conductivity, $w = \mathrm{d}\ln\sigma/\mathrm{d}\ln T$, has proved over recent years to be very helpful in determining the critical value x_c of the metal content x for the metal-insulator transition (MIT). We show that, for various amorphous alloys, recent experimental results on $w(T, x)$ are qualitatively inconsistent with the usual assumptions of continuity of the MIT at $T = 0$ and of $\sigma(T, x_\mathrm{c})$ being proportional to a power of T. These results suggest that $w(T, x_\mathrm{c})$ tends to 0 as $T \to 0$, in which case the MIT should be discontinuous at $T = 0$ (but only there), in agreement with Mott's hypothesis of a finite minimum metallic conductivity.

71.30.+h,71.23.Cq,68.55.-a,81.15.-z

Abbreviations
EDX: energy dispersive X-ray analysis
MIT: metal-insulator transition
MOSFET: metal oxide semiconductor field effect transistor
RBS: Rutherford backscattering analysis

Introduction

Binary amorphous alloys, composed of a semiconductor and a metal, belong to a broad class of materials which exhibit a transition between metallic and activated behaviour of the electrical conductivity caused by the variation of chemical composition, temperature, stress or magnetic field. Other such systems are granular metals, heavily doped crystalline semiconductors, conducting oxides, both amorphous and crystalline, including the high-temperature superconductors, quasicrystals, and doped polymers. Disorder plays an important role in many of these materials. This may involve the structure of an amorphous alloy or the random positions of dopant atoms in an ordered matrix. Simultaneously, various transport properties, in particular the temperature dependence of the conductivity, exhibit the same characteristic qualitative features in many of these substances.

The behaviour of systems that undergo a metal-insulator transition (MIT) has attracted much interest, theoretical as well as experimental, for more than forty years. Milestones were the concepts of Anderson localisation [1], variable-range hopping [2], minimum metallic conductivity [3], the Coulomb glass [4,5], the scaling theory of localisation of noninteracting electrons [6], and the renormalisation group approach incorporating the electron-electron interaction into localisation theory [7,8]. In the literature, many surveys have appeared in this wide area [9–19].

Nevertheless, despite all these efforts, our knowledge about electrical transport in disordered systems in the vicinity of the metal-insulator transition is still rather uncertain. This is strikingly illustrated by two examples: (i) The scaling theory of localisation of noninteracting electrons [6] denies the existence of a MIT in two-dimensional systems. This result was regarded almost as a dogma for many years. Thus, the discovery of a MIT in MOSFETs with very high electron mobility by Kravchenko et al. [20] in 1994 came as a big surprise. (ii) For three-dimensional systems, the value of the critical exponent of the zero-temperature conductivity has been a matter of controversial debate since its first measurements, see e.g. [21–24]. So far, there seems to be no generally accepted solution of this 'critical-exponent puzzle'. Certainly, one of the reasons why this question has not yet been solved, is the uncertainty in identifying the critical concentration in such experiments (see references [25] and [26] commenting on the related publications [23] and [24], respectively).

Among the amorphous systems with a MIT which have been investigated for the last twenty years, metastable alloys of semiconductors with noble metals, transition metals, and rare earths play the most important role. They can be produced by various methods such as thermal and electron-beam evaporation, sputtering, laser quenching, and ball milling. This subject has been investigated so intensively that it is impossible to give here a complete survey of all related studies of structure and transport properties of amorphous alloys in the vicinity of the MIT. Thus the following selection, listed according to the alloys investigated, contains merely the more important publications on low-temperature transport and, in some

cases, structure: Ge-Al [27], Ge-Au [28–30], Ge-Co [31], Ge-Cu [32], Ge-Cr [31,33–35], Ge-Fe [31,36–40], Ge-Mn [31], Ge-Mo [40,41], Ge-Ni [31], Si-Au [42–47], Si-Cr [35,48–57], Si-Fe [38,58,59], Si-Gd [60,61], Si-Mn [58,62–64], Si-Nb [22,65–67], Si-Ni [68–78], Si-Pd [79], Si-Pt [80], Si-Re [81], Si-Ta [82,83], Si-Tb [60], Si-V [84–86], Si-Y [87,88]. The transport studies from this list are not only devoted to conductivity, in particular its temperature dependence, but in many cases also to magnetoresistance; several concern the thermopower too. Moreover, the formation of a Coulomb gap has been studied in various alloys by tunnelling experiments. The structural investigations, e.g. of Si-Fe [38,59] and Si-Ni [68], have demonstrated that the concept of a homogenous amorphous substance is an idealisation. In reality, small (~ 1 nm) clusters with enlarged metal content, with composition close to an intermetallic phase, can be formed. Thus a comparison with related granular systems would be interesting. In particular for Ge-Al, granular films have been studied in detail [89–91]. Besides the substances listed above, several other amorphous materials exhibit a MIT. However, here we refer for comparison only to amorphous InO_x [92–94].

The amorphous semiconductor-metal alloys resemble each other concerning the dependence of the conductivity σ on temperature T and metal content x. The MIT very often occurs for an x value between 0.1 and 0.2. Besides superconductivity in some cases, the only qualitative feature by which these materials may be distinguished from each other seems to be the occurrence of a resistivity dip at low T in the metallic region, observed in some of the alloys only [31]. However, when preparing the same alloy by different technologies, considerable quantitative differences concerning $\sigma(T, x)$ can be present. The typical behaviour of $\sigma(T, x)$, as well as the influence of preparation conditions are represented in Fig. 1 for the system Si-Ni. In trying to understand the differences between the three kinds of samples shown, it is not sufficient only to consider the different amounts of impurities built in from the residual gas, but one has also to take into account structural aspects – note that aging and annealing can considerably change $\sigma(T)$, see e.g. [28,49,58,74]. Therefore, it can be quite problematic to apply theories developed for homogeneous systems to the description of the conduction processes in such alloys. However, due to diverging correlation lengths as the MIT is approached, we can nevertheless hope that there are some universally valid relations in this limit.

The above mentioned uncertainties in the interpretation of experiments by means of current theory, as well as the variability of the structure of seemingly amorphous films suggest that, in interpreting data, one should look for an approach that is as unbiased as possible. It is an important result of recent years that, even on a phenomenological level, such an approach can lead by means of comparatively simple mathematical considerations to interesting conclusions on the character of the MIT. In the next section, we focus on this aspect, analysing the general problems of discriminating between metallic and insulating samples, and demonstrating how useful the logarithmic T derivative of σ can be for this purpose. Then, on the basis of experimental data for various alloys, we shall show that Mott's hypothesis on the existence of a finite minimum metallic conductivity may well be correct after all, at least for certain three-dimensional systems. (For this reason, we shall not discuss fitting of formulae which result from microscopic theories yielding a continuous transition.) In a fourth section, devoted specifically to amorphous $Si_{1-x}Cr_x$, we explain a phenomenological model derived for this substance through searching for universal features in $\sigma(T, x)$, in particular performing a scaling analysis. Finally, after summarising briefly, we

list for future work a series of questions which are implied by this review.

Basic considerations

Consider the electric transport in a (three-dimensional) amorphous alloy as a function of temperature T and a control parameter x, describing the chemical composition. Assume, this alloy undergoes a MIT when x is varied, where σ increases with x. Each study of this MIT needs first of all clear definitions of the terms metal and insulator. To relate them to any finite values of conductivity, temperature and frequency is necessarily an arbitrary judgement. Thus the only unambiguous discrimination between metallic and insulating samples is based on the zero-temperature limit. If the direct current conductivity σ tends to some finite value, then the sample is regarded as metallic; if, however, $\sigma \to 0$ as $T \to 0$, it is insulating. This definition is simple, but it cannot be utilised directly since each measurement has some finite lowest experimentally accessible temperature T_{lea}. Hence, one always depends on an extrapolation. It can be based on a generalisation of experimental experience or on a microscopic theory. Moreover, we can only assume that the physical processes which we have studied within some region of finite T remain the relevant ones down to arbitrarily low T.

In this sense one usually considers a sample with an exponential T dependence of σ,

$$\sigma(T, x) = \sigma_1 \exp\{-[T_0(x)/T]^\nu\}, \tag{1}$$

as insulating at $T = 0$. Here, the exponent ν often has one of the values 1/4 and 1/2 according to variable-range hopping theories by Mott [2] and by Efros and Shklovskii [5], who ignore or take into account electron-electron interaction, respectively; in other cases, ν is determined by fitting. The degree of reliability of this extrapolation approach depends on the width of the σ interval considered. It should enclose several orders of magnitude so that algebraic corrections of Eq. (1) can be neglected. Thus T_{lea} must be considerably smaller than T_0.

On the other hand, samples are considered as metallic if the relation

$$\sigma(T, x) = a(x) + b(x) \cdot T^p \tag{2}$$

with $a > 0$ holds. Mostly, such analyses are performed for $p = 1/2$ or 1/3 resulting from theories by Altshuler and Aronov [95], and Newson and Pepper [96], respectively. The former theory models the superposition of electron-electron interaction and disorder, but it is a perturbation theory so that its applicability close to the transition is at least questionable. The latter theory considers the T-dependent drop of the diffusion constant as the decisive variation, and yields a power law with exponent 1/3 for $x = x_{\text{c}}$ where $a = 0$.

The extrapolation is particularly difficult if a strong, but non-exponential T dependence of σ is observed. In such a case, two interpretations are possible: (i) The sample could be metallic, provided there is a 'good' fit to Eq. (2) with $a > 0$. (ii) The sample could exhibit activated conduction with a small characteristic temperature T_0 being at most of the order of T_{lea}. If, as is generally taken for granted, the parameter T_0 vanishes continuously as the MIT is approached from the insulating side, there is always a finite x interval where the situation (ii) is realized, as visualised by Fig. 2. But, to the best of our knowledge, an appropriate

microscopic theory for a quantitative analysis within this non-exponential (x, T) region is still missing.

Thus, often the samples with an 'intermediate strength of the T dependence' are only analysed in terms of (i), and the alternate possibility (ii) is ignored. However, what one can easily do, and should always do, is to perform a consistency check of the description by Eq. (2). For that, we consider the logarithmic temperature derivative of the conductivity,

$$w(T) = \mathrm{d}\ln\sigma(T)/\mathrm{d}\ln T\,. \tag{3}$$

Its behaviour is qualitatively different on the two sides of the MIT. For insulating samples, Eq. (1) yields,

$$w(T) = \nu\,(T_0/T)^\nu\,, \tag{4}$$

so that $w(T \to 0) = \infty$ for $x < x_\mathrm{c}$. On the other hand, if the conduction is metallic, we get from Eq. (2)

$$w(T) = p\,b\,T^p/(a + b\,T^p)\,. \tag{5}$$

Hence, $w(T \to 0) = 0$ for $x > x_\mathrm{c}$. If this limiting behaviour is not obvious from the experimental data, the validity of Eq. (2) should be questioned. This consistency check was first used for crystalline Si:(P,B), where it showed that the discrimination between insulating and metallic samples, based only on (i), is not satisfactory [25,97]. It proved to be helpful also in several other experiments [64,75,91,94,98].

Note that the consideration of w can even permit a classification, when a sample belongs to the x region where the activated character cannot be detected via exponential $\sigma(T)$, i.e. where $w \lesssim \nu$. Assume, for a certain sample, we have observed that $\mathrm{d}w/\mathrm{d}T \leq 0$ at T_lea. Experimental experience (see next section) seems to suggest that, once w has begun to increase with decreasing T, it continues to do so as T tends to 0. If, therefore, we extrapolate merely the validity of $\mathrm{d}w/\mathrm{d}T \leq 0$ to arbitrarily low T, we reach the conclusion that, as $T \to 0$, σ vanishes at least as fast as some (positive) power of T. Thus the observation of $\mathrm{d}w/\mathrm{d}T \leq 0$ at T_lea suggests strongly that the sample is an insulator at $T = 0$.

In this way, the calculation of w allows us to check whether small deviations of the experimental data from the fit of Eq. (2) are understandable as random scatter of the data points, or as some small correction, or whether they indicate a qualitative change to be expected if lower temperatures were accessible. Inspection of w also provides a sensible accuracy test concerning thermometry problems and thermal decoupling. Sudden changes of w occurring for all samples at roughly the same T value, for example, should be investigated with care, cf. [54].

However, the analysis of w cannot only be used in classifying a given sample as metallic or activated. This quantity contains still more information [78]: A fingerprint of the character of the MIT at $T = 0$ can be contained in the graph of $w(T, x = \mathrm{const.})$ for a set of samples measured at finite T. To illustrate this, we calculate $w(T, x)$ for two simple, qualitative models. On the basis of 'usual' T dependences, they are constructed so that continuity of σ at x_c for arbitrary finite T and monotonicity of $\sigma(T = \mathrm{const.}, x)$ are guaranteed.

First we assume the transition to be continuous also at $T = 0$:

$$\sigma(T, x) = \begin{cases} T^{1/2} \exp\{-[T_0(x)/T]^{1/2}\} & \\ a(x) + T^{1/2} & \end{cases} \quad \text{for} \quad \begin{array}{l} x < x_{\mathrm{c}} \\ x \geq x_{\mathrm{c}} \end{array}, \tag{6}$$

where $T_0(x \to x_{\mathrm{c}} - 0) = 0$, and $a(x \to x_{\mathrm{c}} + 0) = 0$. For simplicity, all quantities are dimensionless. Corresponding $w(T)$ curves are presented in Fig. 3: The curve, which separates activated and metallic regions, is a straight line parallel to the T axis, $w(T, x_{\mathrm{c}}) = p = 1/2$. There are no pieces of 'insulating' $w(T)$ curves with $w < p$. Note that, if $w < p$, always $\mathrm{d}w/\mathrm{d}T > 0$.

Next we assume the transition to be discontinuous, but only at $T = 0$:

$$\sigma(T, x) = \begin{cases} (1 + T^{1/2}) \exp\{-[T_0(x)/T]^{1/2}\} & \\ a(x) + T^{1/2} & \end{cases} \quad \text{for} \quad \begin{array}{l} x < x_{\mathrm{c}} \\ x \geq x_{\mathrm{c}} \end{array}, \tag{7}$$

where $T_0(x \to x_{\mathrm{c}} - 0) = 0$, and $a(x \to x_{\mathrm{c}} + 0) = 1$. Fig. 4 shows corresponding $w(T)$ curves. In contrast with Fig. 3, in the activated region, this graph exhibits minima of $w(T, x = \mathrm{const.})$, where the values of $w_{\min}(x)$ become much smaller than p as the MIT is approached. This feature arises from the limiting behaviour of $w_{\min}(x)$ and of the related $T_{\min}(x)$ as $x \to x_{\mathrm{c}} - 0$; both these quantities tend to zero. We would like to emphasise that, therefore, Fig. 4 exhibits also such 'insulating' $w(T)$ curves which have low-T pieces where simultaneously $\mathrm{d}w/\mathrm{d}T < 0$ and $w < p = 1/2$ hold. Moreover, $w(T, x_{\mathrm{c}}) = T^{1/2}/[2(1 + T^{1/2})]$ tends to 0 as $T \to 0$.

The correlation between $w(T, x_{\mathrm{c}})$ vanishing as $T \to 0$ and $\sigma(0, x)$ jumping at x_{c} is not a special feature of the model (7) we have used. We can demonstrate this by examining the consequences of the limiting behaviour of w. Assume, at the MIT, w tends to 0 according to some power law as $T \to 0$,

$$w(T, x_{\mathrm{c}}) = c\,T^q, \tag{8}$$

where $q > 0$. Hence,

$$\sigma(T, x_{\mathrm{c}}) = \sigma(0, x_{\mathrm{c}})\,\exp(c\,T^q/q). \tag{9}$$

The exponential factor is finite for arbitrary T so that obtaining a finite value of σ at any measuring temperature T_{m} for $x = x_{\mathrm{c}}$ indicates that $\sigma(0, x_{\mathrm{c}})$ is finite as well, and that, since $\sigma(0, x) = 0$ for $x < x_{\mathrm{c}}$, the function $\sigma(0, x)$ must have a discontinuity at x_{c}.

Experimental results on $w(T, x)$

In the previous section, we have explained how the logarithmic derivative $w(T, x)$, defined by Eq. (3), yields valuable information on the MIT without the need of performing fits to a microscopic theory. Now we consider five materials from this point of view.

A detailed study, using this approach, of amorphous $\mathrm{Si}_{1-x}\mathrm{Ni}_x$ [78] was recently published, cf. Fig. 1. Within this investigation, sample sets prepared by two different preparation technologies were compared. Figs. 5 and 6 show part of the $w(T)$ data obtained in [78]. In these graphs, as well in Figs. 7–10, w is represented versus $T^{1/2}$ in order to stretch the low-T in comparison to the high-T part. Moreover, for the samples with $w \ll 1/2$, w would be approximately proportional to $T^{1/2}$, if, as often assumed, Eq. (2) with $p = 1/2$ would hold.

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For both data sets presented in Figs. 5 and 6, at sufficiently high T, all samples studied behave very similarly: $w(T)$ increases with increasing T. On the other hand, for the samples with the smallest Ni content, at low T, there is a pronounced increase of $w(T)$ with decreasing T, indicating activated conduction. The strength of this contribution decreases with increasing x. One common feature of all samples (with $w > 0$), which exhibit such an increase of w with decreasing T, has to be stressed: this increase is always found to continue down to the lowest accessible T. The generalisation of this finding is a basic assumption of our data analysis.

The differing behaviour at low and high T must be caused by two different mechanisms being dominant at low and high T, respectively. The low-T mechanism related to increasing $w(T)$ as T decreases is very likely a kind of hopping conduction, cf. [48,49,76,101]. Concerning the high-T contribution it was speculated in [49] that electron-phonon interaction might be the origin.

The minimum of $w(T)$ related to the crossover between these two mechanisms is particularly interesting. It is located at $T_{min} = 150$ K for the most insulating sample studied, and shifts to lower T with increasing Ni content. Whatever the character of the MIT at $T = 0$, this behaviour has to be expected: if, as is generally taken for granted, the characteristic hopping energy tends to 0 as the transition is approached, hopping only becomes dominant at lower and lower T. However, what provides information on the character of the MIT is the behaviour of the related w_{min}. This quantity also seems to tend to 0 as $x \to x_c - 0$: For the samples 1, 2, d, and e, $T_{min} = 6$ K, 4 K, 0.8 K, and 0.2 K, respectively, where $w_{min} = 0.42, 0.32, 0.15$, and 0.06.

Figs. 5 and 6 also show that $w(T = \text{const.}, x)$ decreases monotonically as the MIT is approached from the insulating side (consider in particular the series a–h in Fig. 5). Thus $w(T, x_c)$ must be smaller than $w(T)$ for that insulating sample which is closest to the MIT. In that sense, the function $w_{min}(T_{min})$ is an upper bound of $w(T_{min}, x_c)$, and the probable simultaneous vanishing of T_{min} and w_{min} as $x \to x_c - 0$ imply that $w(T, x_c) \to 0$ as $T \to 0$. Therefore, according to the previous section, the limit $\sigma(T \to 0, x_c)$ appears to be finite. It has the meaning of a minimum metallic conductivity because $\sigma(T = \text{const.}, x)$ monotonically increases with x. Thus the MIT is very likely discontinuous at $T = 0$. For a more detailed discussion see [78].

It might be worth mentioning a technical point in connection with Figs. 5 and 6. The comparatively small random scatter of these $w(T)$ data arises not only from a high accuracy of the $R(T)$ measurements, but also from the numerical method used for calculating w. If we consider $\ln \sigma$ as function of $\ln T$, its slow variation permits a piecewise approximation of high accuracy as a second-order polynomial in $\ln T$. Thus, in [78], a window taking in a certain number, k, of neighbouring points was moved along the $\ln \sigma(\ln T)$ curve, and w was calculated by means of linear regression from the data within the window. The trick is to relate the obtained slope to that $\ln T$ value for which the derivative of a second-order polynomial is exactly reproduced, independently of the values of its coefficients,

$$\ln T_{lf} = \frac{k \sum_i (\ln T_i)^3 - \sum_i \ln T_i \sum_j (\ln T_j)^2}{2(k \sum_i (\ln T_i)^2 - (\sum_i \ln T_i)^2)} \, , \tag{10}$$

where the sums run over all points within the window considered. In this way, the total error (numerical plus random) can be kept small. Finally, if a set of $w(T)$ data has been

calculated by simply using pairs of neighbouring $\sigma(T)$ points, the above procedure can be emulated by smoothing with appropriately chosen weights. This equivalence will be utilised below in analysing $w(T)$ data from the literature.

We turn now to comparison with other alloys. Amorphous $Si_{1-x}Cr_x$ prepared by electron-beam evaporation was studied in [48–52]. Fig. 7 shows $w(T)$ for four samples, obtained from $\sigma(T)$ data published in [48,49]. Below roughly 20 K, activated conduction is obvious for three of them from the behaviour of dw/dT. Again, there are minima in the related $w(T)$, and these $w(T)$ take also values which are far smaller than $1/2$.

Recent results on amorphous $Si_{1-x}Mn_x$ by Yakimov et al. (see Fig. 4 of [64]), corroborate the qualitative behaviour of $w(T, x)$ which we have presented for amorphous $Si_{1-x}Ni_x$ and $Si_{1-x}Cr_x$. In Fig. 8 here, we show $w(T)$ relations obtained by smoothing the original $Si_{1-x}Mn_x$ data according to the procedure mentioned above.

From the examples presented, the question may arise as to whether the existence of low-T pieces of $w(T)$ curves with simultaneously $w \ll 1/2$ and $dw/dT \leq 0$ – very likely caused by a discontinuity of $\sigma(0, x)$ at x_c – is specific for (some) alloys of semiconductors with transition metals only. That this is not the case is shown by the following two examples. Fig. 9 presents two $w(T)$ curves for samples of amorphous InO_x (data from Figs. 8 and 9 of [94]). These samples seem to exhibit activated conduction although w is very small, i.e., of the order of 0.01. Thus the carrier concentration must be close to its critical value in both cases. Fig. 10 shows $w(T)$ curves for three Ge-Al samples (data from Fig. 2 of [91]). Although these samples do not have an amorphous structure, but consist of small ($\lesssim 20$ Å) Al grains embedded in an amorphous matrix, $w(T, x)$ exhibits the typical features found with the amorphous materials studied above. Thus clustering seems not to destroy this qualitative behaviour, though it may change the value of the minimum metallic conductivity.

To summarise, for all the five materials considered, the qualitative behaviour of $w(T, x)$ does not appear to be consistent with the usual assumption that the MIT is continuous at $T = 0$, and that $\sigma(T, x_c) \propto T^p$ with $p = 1/2$ or $1/3$. It suggests that $w(T, x_c)$ tends to 0 as $T \to 0$, in which case, according to the arguments presented earlier, the MIT should be discontinuous at $T = 0$ (but only there).

Phenomenological model of $\sigma(T, x)$

The analysis in the previous section has illuminated a qualitative feature of the MIT in amorphous alloys: for several materials, it seems likely that there is a finite minimum metallic conductivity. However, for identification of physical mechanisms, quantitative descriptions are needed, where homogenous systems have first of all to be understood. Highly stable amorphous alloys, in which the formation of crystalline regions proceeds exceptionally slowly, are particularly suitable for this. They offer the best chances for observing the corresponding dependences in an almost clean form. Such a substance is amorphous $Si_{1-x}Cr_x$, which is used in microelectronics as a basis material of thin-film resistors [57].

Amorphous $Si_{1-x}Cr_x$ films prepared by electron-beam evaporation have been investigated in [48–52]. A particularly important result of these studies is the detection of a scaling law for the T dependence in the hopping region. For $T \lesssim 20$ K, the conductivity can be described by

$$\sigma(T, x) = \sigma_0 \cdot \varphi(T/T_0(x)) . \tag{11}$$

This universality was detected by two ansatz-free methods: (i) graphical construction of a master curve [48], see Fig. 11, and (ii) proving that $w = \mathrm{d}\ln\sigma/\mathrm{d}\ln T$ is completely determined merely by $\ln\sigma$ (see Fig. 2 in [49]), i.e., by demonstrating that, in a w versus $\ln\sigma$ plot, the data points from different samples form a common curve. The validity of the scaling law (11) has an important physical meaning: it shows that a single mechanism governs the conduction. Note, that this general result was obtained without performing fits of an ansatz based on microscopic theory.

For high temperatures, i.e., as $T/T_0 \to \infty$, the function $\varphi(T/T_0)$ seems to saturate [49]. Therefore, it is suggested to eliminate the ambiguity of Eq. (11) concerning the value of σ_0 by defining $\varphi(\infty) = 1$. On the other hand, in the exponential region, Eq. (11) takes the form of Eq. (1) with $\nu \approx 0.5$ – an indication of the relevance of electron-electron interaction – see [48,49]. It follows from the scaling law that the related pre-factor σ_1 is independent of x. This seems to be the case also in several other substances [13], cf. [101]. It is remarkable that σ_1 is by a factor of 2.5 smaller than σ_0 [49].

This scaling behaviour is broken in two ways. On the one hand, increasing the temperature above roughly 20 K (the specific value depends on the accuracy demanded) causes a faster increase of σ than expected according to extrapolation by means Eq. (11). It is remarkable that this feature can be described by a multiplicative decomposition,

$$\sigma(T,x) = \sigma_0 \cdot \varphi(T/T_0(x)) \cdot \xi(T,x), \tag{12}$$

with $\xi(0,x) = 1$: In [49], it was observed that the high-T factor $\xi(T,x)$ is almost independent of x close to the MIT, and that it depends on T almost linearly between roughly 100 and 300 K. Given this independence of x, the high-T deviations from the scaling law (11) probably originate from a single mechanism, which, due to the continuity of $\sigma(T = \text{const.}, x)$ at x_c for $T > 0$, seems to 'survive' the MIT. The nature of this mechanism is unclear as yet; it was speculated in [49] that electron-phonon interaction could play an important role. On the other hand, annealing the samples causes changes of the pre-factor σ_1 in the hopping law (1) [49], and, for sufficiently high annealing temperature, even the value of the exponent ν seems to be shifted. This arises presumably from a second length scale becoming relevant, namely the size of $CrSi_2$ clusters formed [55].

Also, in the metallic region, a high-T mechanism (presumably the same as on the activated side) plays a substantial role. Here, it competes with a low-T mechanism which causes the opposite behaviour, i.e., an increase of σ with decreasing T. In [51], the detailed study of this low-T contribution was made possible by a trick: Starting from the observation that, in a related graph, the $\sigma(T)$ curves of the individual samples are almost parallel to each other at high T, the difference between the σ values of the sample under consideration and a reference sample was calculated. Assuming additivity of the σ contributions related to the different mechanisms, this procedure considerably reduces the influence of the high-T mechanism, and thus magnifies the low-T contribution. Therefore the latter could be studied within a broader T interval. A series of power-law fits of this difference were performed in [51] to determine the exponent p in Eq. (2). In doing so, unphysical dependences of the p value on the bounds of the T and x regions considered were carefully excluded. The fits which simultaneously took into account 15 samples yielded $p = 0.19 \pm 0.03$. Finally, in [52], the analysis of the correlations between the parameters a and b of the approximation (2) lead to the following empirical description of $\sigma(T,x)$ in the metallic region:

$$\sigma(T, x) = a(x) + b(x) \cdot T^p + \sigma_0 \cdot \xi(T, x), \tag{13}$$

where $b \leq 0$. The relation between the parameters a and b exhibits the singularity

$$b \propto a^\vartheta \tag{14}$$

with the critical exponent $\vartheta = 0.68 \pm 0.05 - (p - 0.19)$. Since a^ϑ is not defined for $a < 0$, this singularity can be considered as another independent indication of the MIT.

Equations (12) and (13) together form a simple phenomenological model of $\sigma(T, x)$ close to the MIT. Guaranteeing continuity at x_c for $T > 0$, they describe both sides of the transition. For further details, in particular small low-T deviations and consequences from this model, we refer to [52].

Conclusions

Summarising, we have analysed $\sigma(T, x)$ data from several amorphous alloys close to the MIT in an as unbiased way as possible, avoiding the use of results from current microscopic theories to a large extent. For that, we have considered the T dependence of the logarithmic temperature derivative of the conductivity, $w(T, x) = \mathrm{d} \ln \sigma / \mathrm{d} \ln T$. In various cases, the behaviour of this quantity differs qualitatively from the predictions obtained from commonly accepted theory. There are samples, for which w simultaneously takes values far smaller than $1/2$, and then increases with decreasing T down to the lowest temperatures studied. Hence, it is suggested that $w(T, x_c)$ tends to 0 as $T \to 0$. This limiting behaviour indicates a discontinuity of $\sigma(0, x)$, so that Mott's hypothesis of the existence of a finite minimum metallic conductivity is probably correct in these systems after all. However, it does not imply a discontinuity of $\sigma(T = \mathrm{const.}, x)$ at the MIT for any $T > 0$, neither does it permit any conclusion as regards the validity of the arguments Mott used to estimate a value for minimum metallic conductivity. Hence, we believe that, for amorphous alloys, the 'critical-exponent puzzle' concerns only an artifact arising from unphysical fitting.

For amorphous $\mathrm{Si}_{1-x}\mathrm{Cr}_x$, a comparatively stable alloy, one can go on, and derive a quantitative phenomenological model by searching for universal features in $\sigma(T, x)$ [48–52]. On the activated side of the MIT, a scaling law for the temperature dependence, $\sigma(T, x) = \sigma_0 \cdot \varphi(T/T_0(x))$, is the basis of this model. However, annealing destroys the scaling behaviour so that a highly amorphous structure seems to be the necessary prerequisite for this universality. On the metallic side, a negative $\sigma(T)$ contribution proportional to T^p with $p = 0.19 \pm 0.03$ governs the low-temperature behaviour. The related proportionality factor vanishes as the MIT is approached. It is remarkable that, in the exponential region, the above scaling law can also be observed in several other substances [101,13].

Comparing the characteristic features of this phenomenological model with basic assumptions of and conclusions from current microscopic theories permits speculations on the physical nature of the MIT in these systems, see [13,99]. It is particularly important that the model yields $\mathrm{d}\sigma/\mathrm{d}T = 0$ at x_c for sufficiently low T. According to [13,99], the MIT cannot be understood in terms of an Anderson transition, but it should be caused by the breakdown of screening when the MIT is approached from the metallic side. This should be accompanied by the formation of a Coulomb gap having the width 0 at x_c and opening when moving into the insulating x region. Our speculation on the nature of the MIT coincides with the microscopic theory very recently published by Chitra and Kotliar [102]. These

authors incorporate the long-range Coulomb interaction into dynamical mean-field theory, and obtain that the MIT should be discontinuous in two- and three-dimensional systems.

In conclusion, the review given above should not be understood as a 'final' solution concerning the character of the MIT in amorphous alloys. Instead, our aims have been to demonstrate by an unbiased analysis that this topic cannot be considered as closed, and to stimulate further research. There are several interesting questions for future experiments: (i) How does $w(T)$ behave for other alloys? Is the existence of samples with simultaneously $w \ll 1/2$ and $\mathrm{d}w/\mathrm{d}T < 0$ being valid down to the lowest measuring temperatures indeed a general feature? (ii) Following [31], under which conditions does one observe metallic $\sigma(T)$ curves with $\mathrm{d}\sigma/\mathrm{d}T < 0$? This means what influence have composition, magnetic moments, structure, and preparation conditions on this phenomenon, and on the bounds of the T interval where this mechanism is dominant? (iii) Can the phenomenological model, which was obtained for amorphous $Si_{1-x}Cr_x$, also be used for the description of other comparatively stable amorphous alloys? In particular, is the scaling function $\varphi(T/T_0(x))$ for the non-exponential region substance independent as, provided there is no clustering, it seems to be in the exponential region [13]? What about the T exponent in the metallic region? (iv) Can this model be extended to the description of other quantities such as the magnetoresistance? (v) Last, but not least, it should be noted that the conclusions drawn above are very different from the description of heavily doped crystalline semiconductors given in a previous review in this journal, i.e., in [19]. On the other hand, Fig. 1 of [97] and Fig. 6 of [100] show for crystalline Si:(P,B) and Si:As, respectively, that the behaviour of $w(T)$ resembles the results for amorphous alloys. How can these contradictions be resolved?

Acknowledgements

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FIGURES

FIG. 1.   Overview of $\sigma(T, x)$ for a-Si$_{1-x}$Ni$_x$ based on data from [78,77]. The samples 1–5 (+) were prepared by electron-beam evaporation of the alloy [78], the samples e and f ($\bullet$) were deposited by a gradient technique based on co-evaporation of the elements [78], and the samples α and β ($\blacktriangle$) were sputtered [77]. Ni content: $x = 0.149$, 0.164, 0.167, 0.189, 0.221 (RBS) for samples 1–5, respectively; $x = 0.235$, 0.248 (EDX, these values exceed related RBS data by roughly 0.06 [78]) for samples e and f, respectively; $x = 0.207$, 0.271 (EDX) for samples α and β, respectively.

FIG. 2.   Experimental parameter plane: The insulating region, where only activated conduction occurs, is marked by I, the metallic region by M, and the lowest experimentally accessible temperature by T_{lea}. The characteristic hopping temperature, $T_0(x)$, is represented by a full line. Measuring $\sigma(T, x = \text{const.})$ means to obtain data points ($\bullet$, $\times$) along vertical lines. Only for $T < T_0$ does σ depend exponentially on T. For $T > T_0$, comparatively flat, non-exponential $\sigma(T)$ dependences are expected. Thus, for $\bullet$, depending on T, both exponential and non-exponential behaviour is observed. However, for $\times$, only non-exponential $\sigma(T, x = \text{const.})$ is found, although this sample belongs to the insulating region, too. The latter problem occurs in the whole interval $[x^\star, x_c)$. (Slightly modified reproduction of Fig. 1 from [78].)

FIG. 3.   Logarithmic derivative $w(T, x) = \mathrm{d}\ln\sigma/\mathrm{d}\ln T$ for a continuous transition according to Eq. (6). The (at $T = 0$) insulating region is marked by I, the metallic region by M. The dashed line represents the separatrix between these areas. The full lines correspond to the following parameter values: $T_0(x)^{1/2} = 0.03$, 0.1, 0.3, 1 in the insulating region, and $a(x) = 0.03$, 0.1, 0.3, 1 in the metallic area.

FIG. 4.   Logarithmic derivative $w(T, x) = \mathrm{d}\ln\sigma/\mathrm{d}\ln T$ for a discontinuous transition according to Eq. (7). The full lines correspond to the following parameter values: $T_0(x)^{1/2} = 0.02$, 0.06, 0.2, 0.6 in the insulating region, and $a(x) - 1 = 0.2$, 0.6, 2, 6 in the metallic area. For further details see caption of Fig. 3.

FIG. 5. $w(T, x) = \mathrm{d}\ln\sigma/\mathrm{d}\ln T$ for a-Si$_{1-x}$Ni$_x$, presenting data from Figs. 7a and 7b of [78]. Ni content: $x = 0.149$, 0.164 (RBS) for samples 1 and 2, respectively; $x = 0.195$, 0.203, 0.212, 0.223, 0.235, 0.248, 0.264, 0.282 (EDX, these values exceed related RBS data by roughly 0.06 [78]) for samples a–h, respectively.

FIG. 6.   Low-T / low-w part of Fig. 5. The data presented were obtained from measurements in three different cryostats, where several months passed between the investigations. Samples g and h are metallic films [78], included for comparison; for sample f, a conclusion on the character of the conduction could not be drawn within [78]. (Modified reproduction of Fig. 8b from [78].)

FIG. 7. $w(T, x) = \mathrm{d}\ln\sigma/\mathrm{d}\ln T$ for a-Si$_{1-x}$Cr$_x$, obtained from data published in [48,49] (mainly given in Fig. 3 of [49]). Cr content: $x = 0.109$ ($\circ$), 0.127 ($\times$), 0.149 (+), and 0.193 ($\triangle$). The sample marked by $\triangle$ is a metallic one included for comparison.

FIG. 8. $w(T, x) = \mathrm{d}\ln\sigma/\mathrm{d}\ln T$ for a-Si$_{1-x}$Mn$_x$, obtained from the $w(T, x)$ data published in Fig. 4 of [64]. The T dependences are smoothed here, see text, using windows of 15, 15, and 45 points for $x = 0.15$, 0.17, and 0.22, respectively.

FIG. 9. $w(T, x) = \mathrm{d}\ln\sigma/\mathrm{d}\ln T$ for a-InO$_x$, obtained from data published in Figs. 8 ($\sigma(T)$ for sample 3) and 9 ($w(T)$ for sample 42) of [94]. Here, $w(T)$ was calculated using windows of 4 and 5 points for sample 3 (+) and sample 42 (■), respectively.

FIG. 10. $w(T, x) = \mathrm{d}\ln\sigma/\mathrm{d}\ln T$ for granular Ge$_{1-x}$Al$_x$, based on $w(T, x)$ data from Fig. 2 of [91]. The corresponding $R(T)$ measurements were performed in a magnetic field of 3.5 T to suppress superconductivity effects. Here, $w(T)$ was smoothed using windows of 3 points.

FIG. 11. Test of scaling behaviour of $\sigma(T, x)$ for a-Si$_{1-x}$Cr$_x$ by means of the construction of the master curve (full line) of the $\sigma(T)$ relations (dashed) for ten samples, taken from Fig. 4 of [48]. (For one of the samples, a thickness inaccuracy is corrected here.) The dashed-dotted curve represents the asymptotic exponential behaviour, $\sigma \propto \exp[-A\,(T_0/T)^{1/2}]$ (the constant A arises from the arbitrariness in fixing the T scale of the mastercurve).
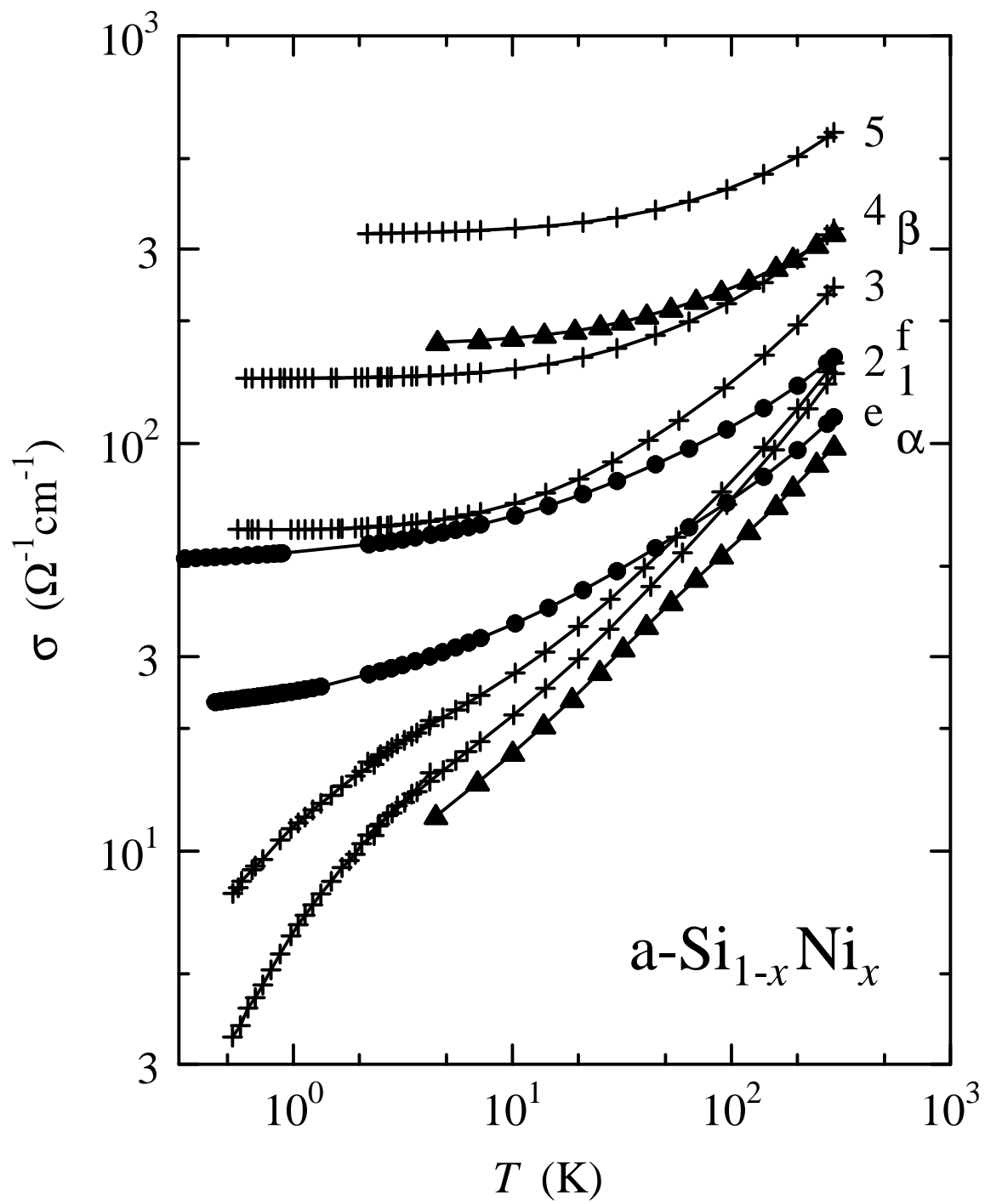
Fig. 1
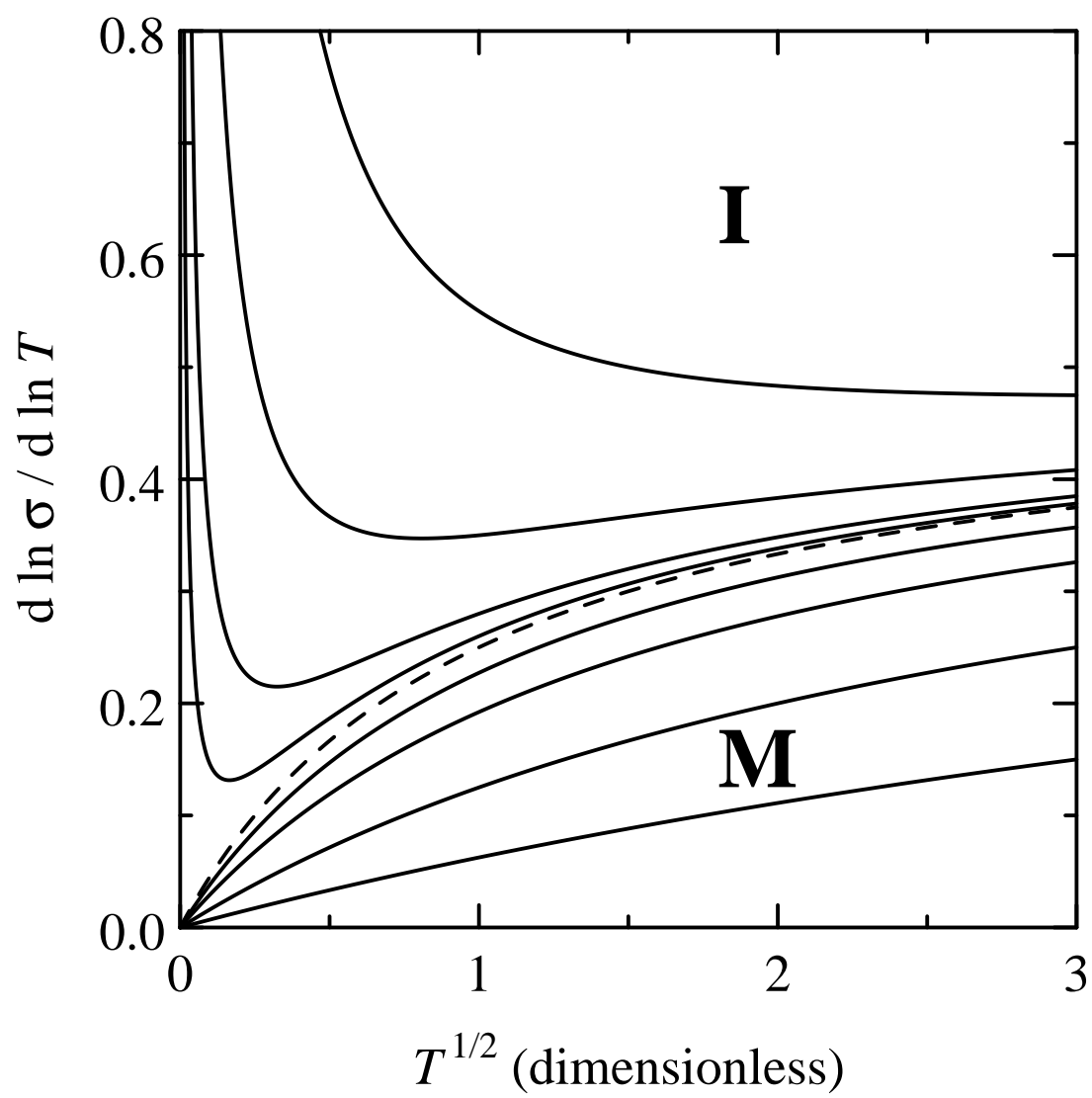
(Mö / Adk)
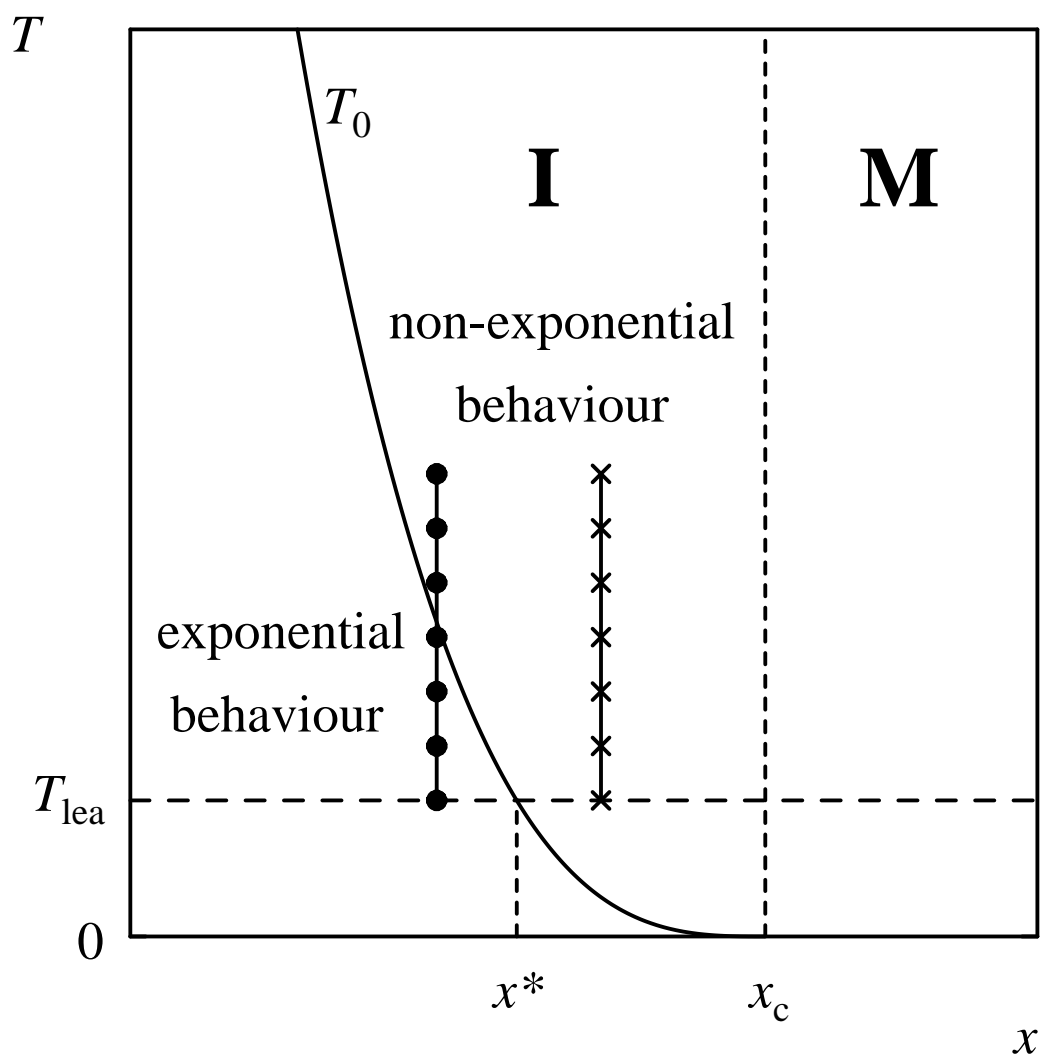
Fig. 2

(Mö / Adk)
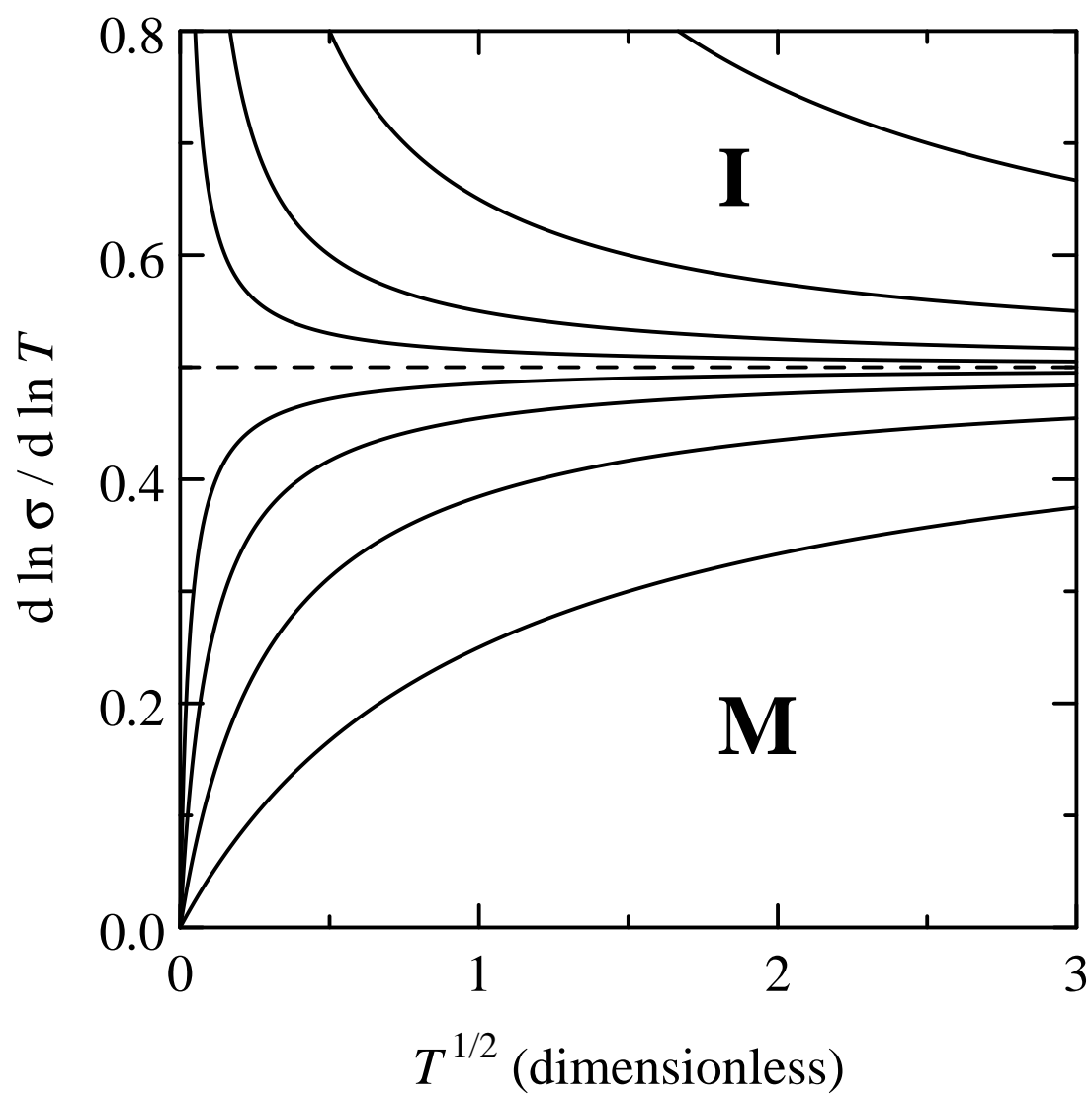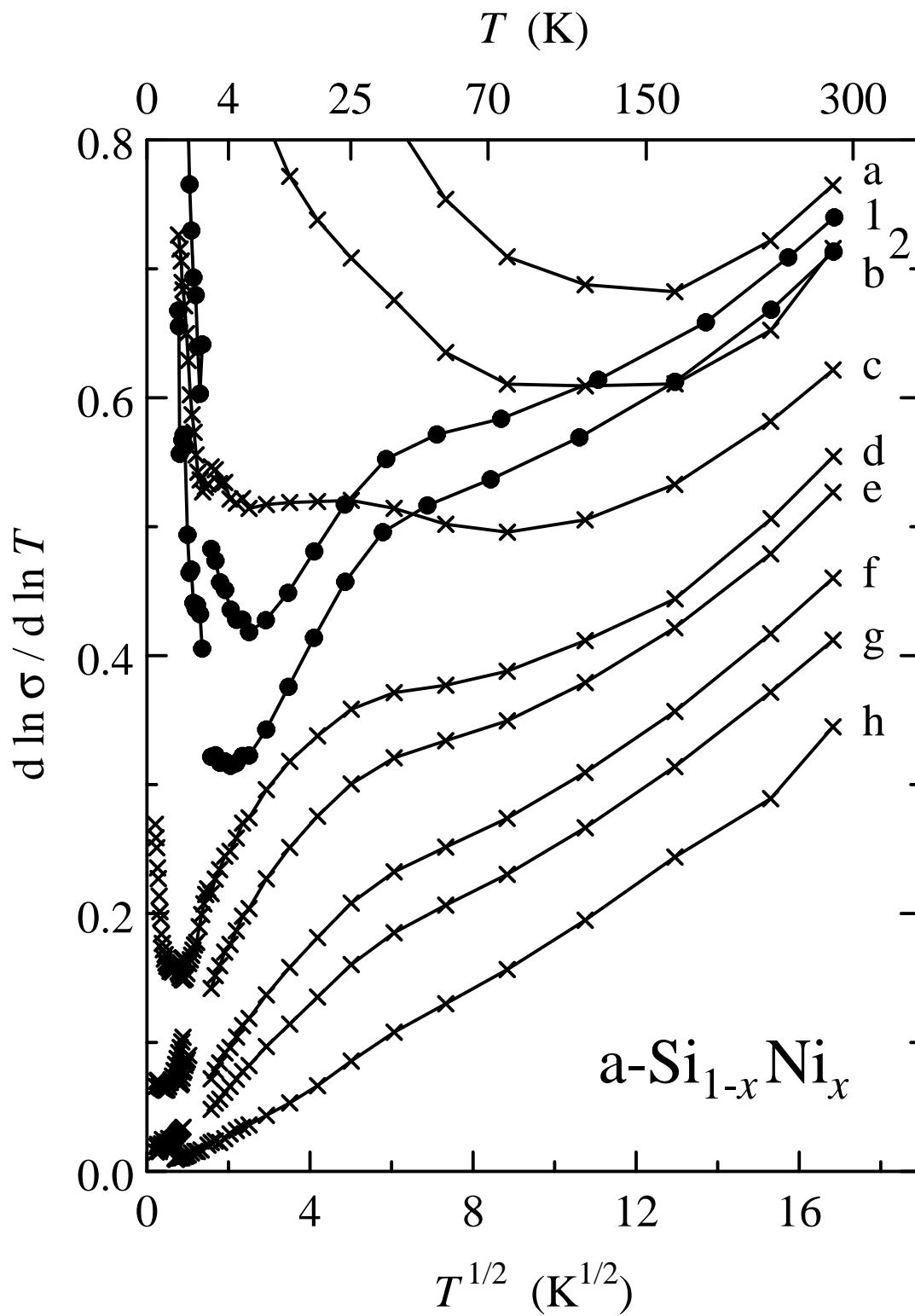
Fig. 3

(Mö /Adk)

Fig. 4
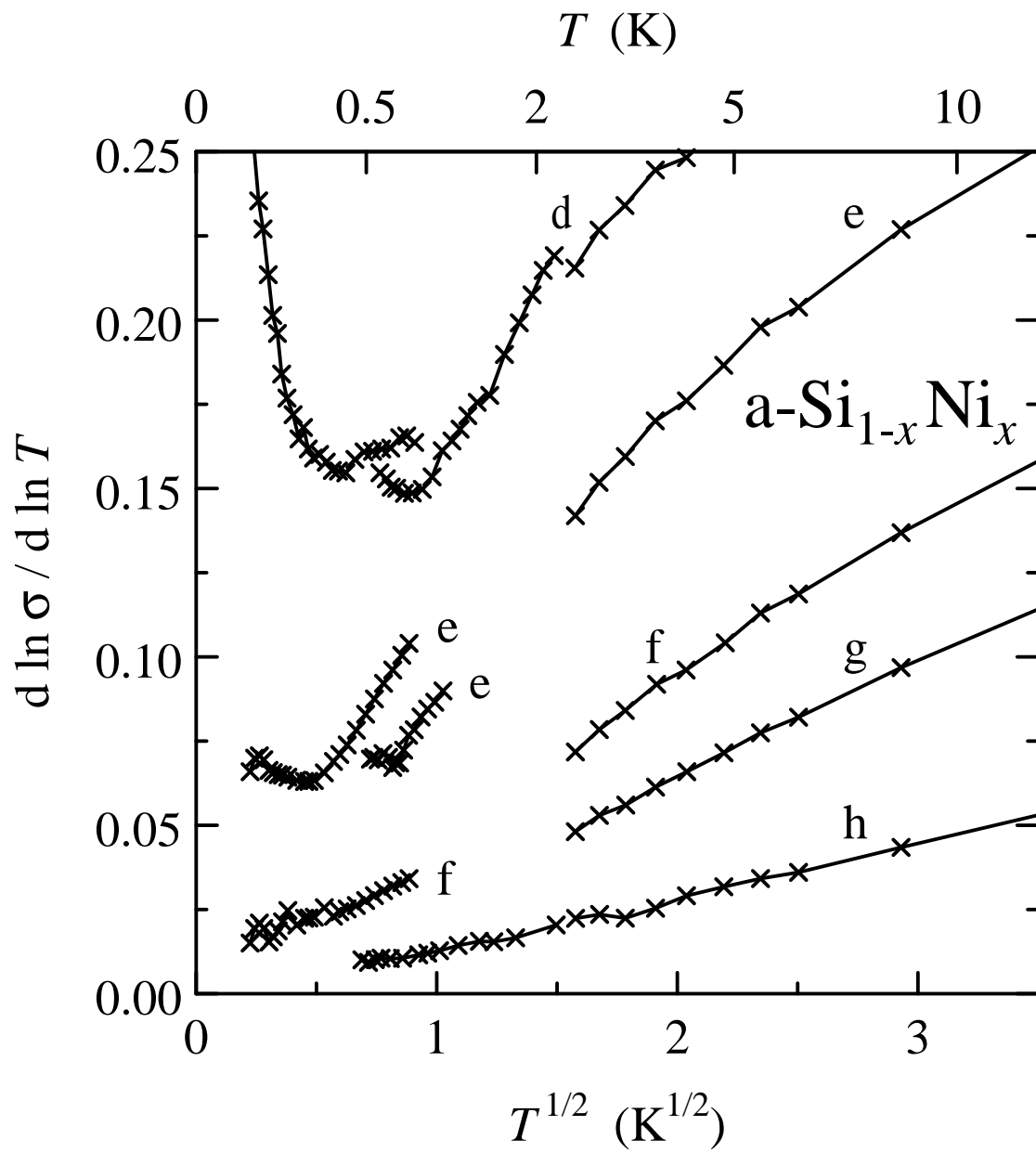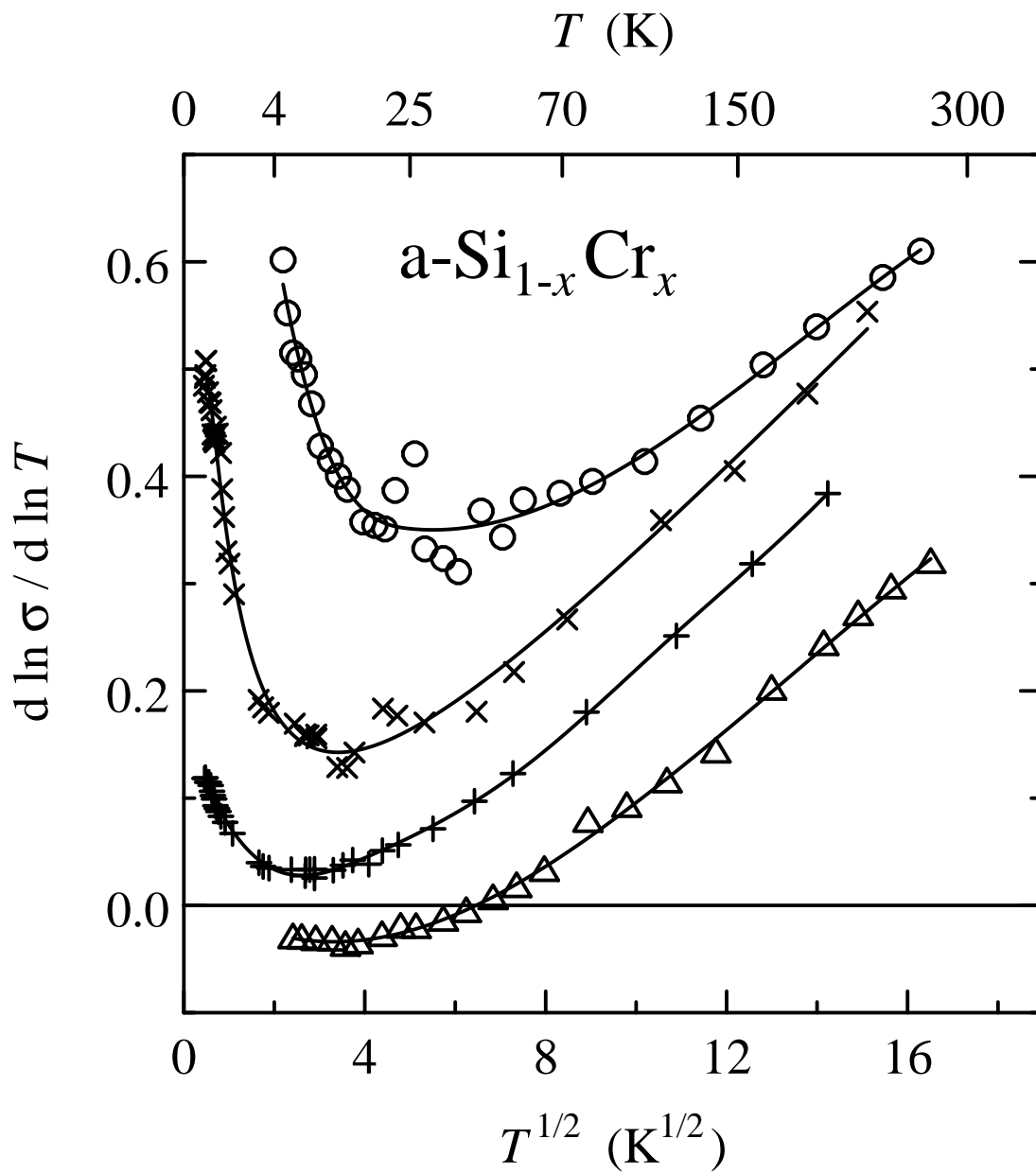
(Mö /Adk)

Fig. 5

(Mö / Adk)
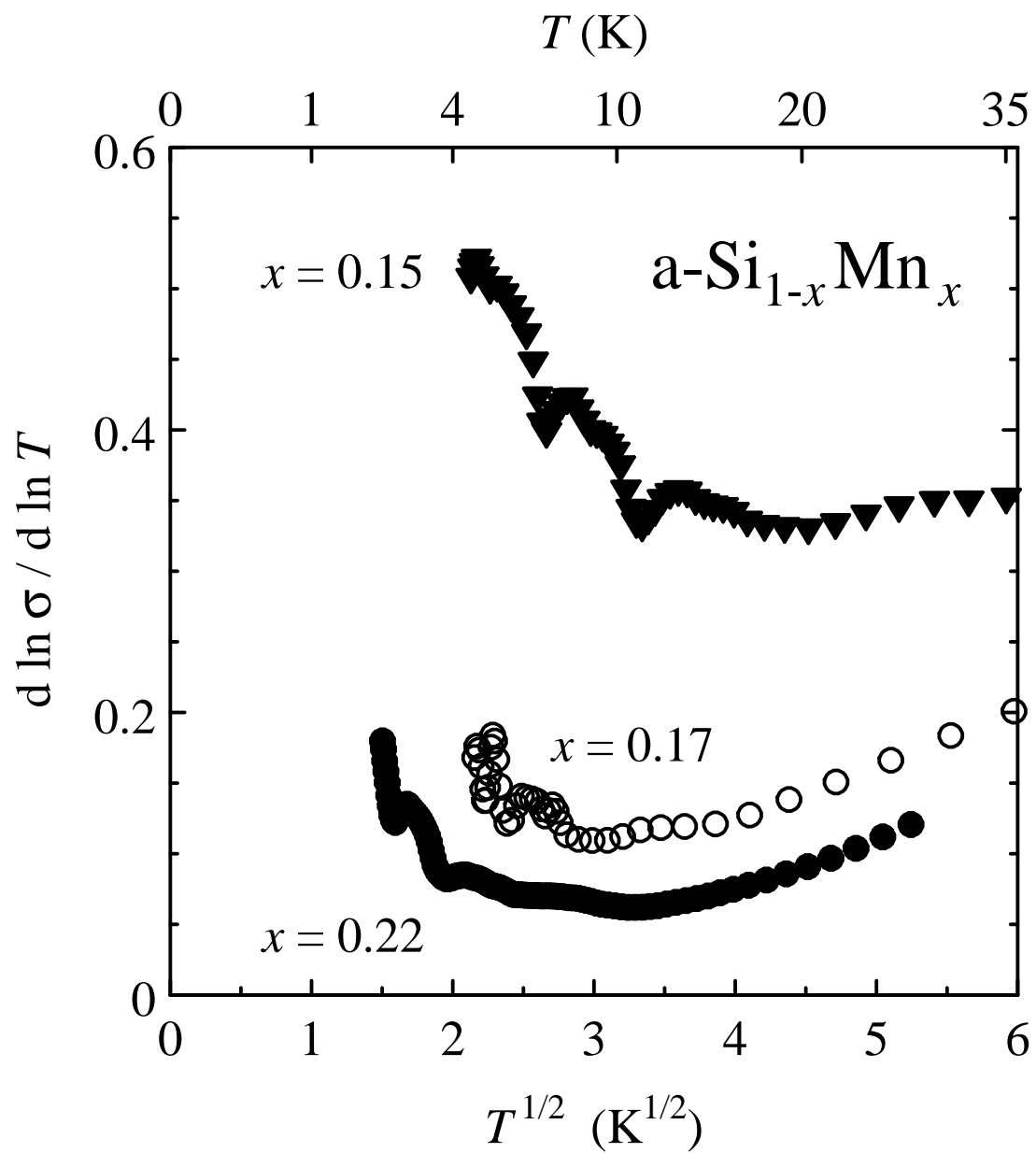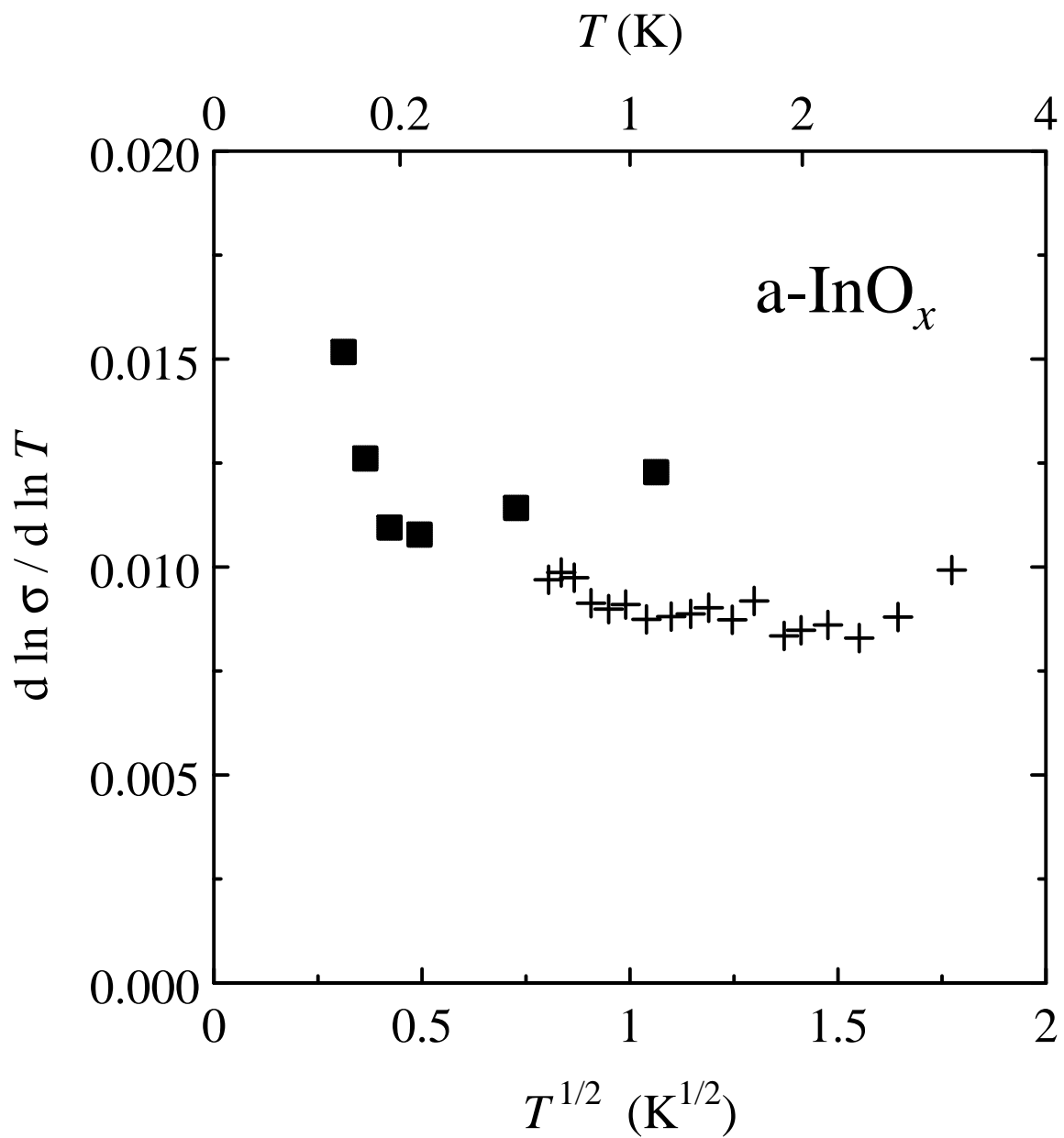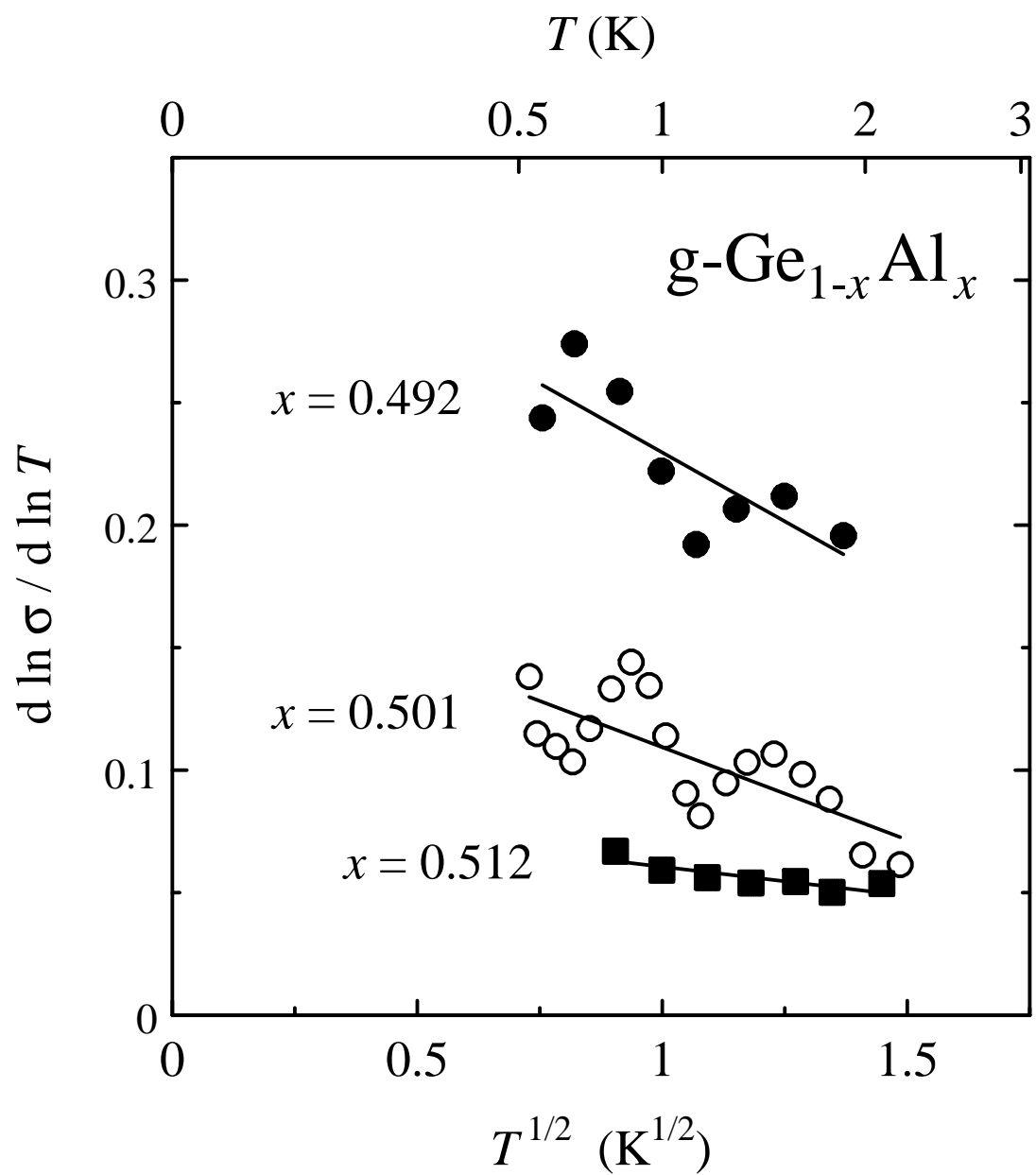
Fig. 6

(Mö / Adk)

Fig. 7

(Mö / Adk)

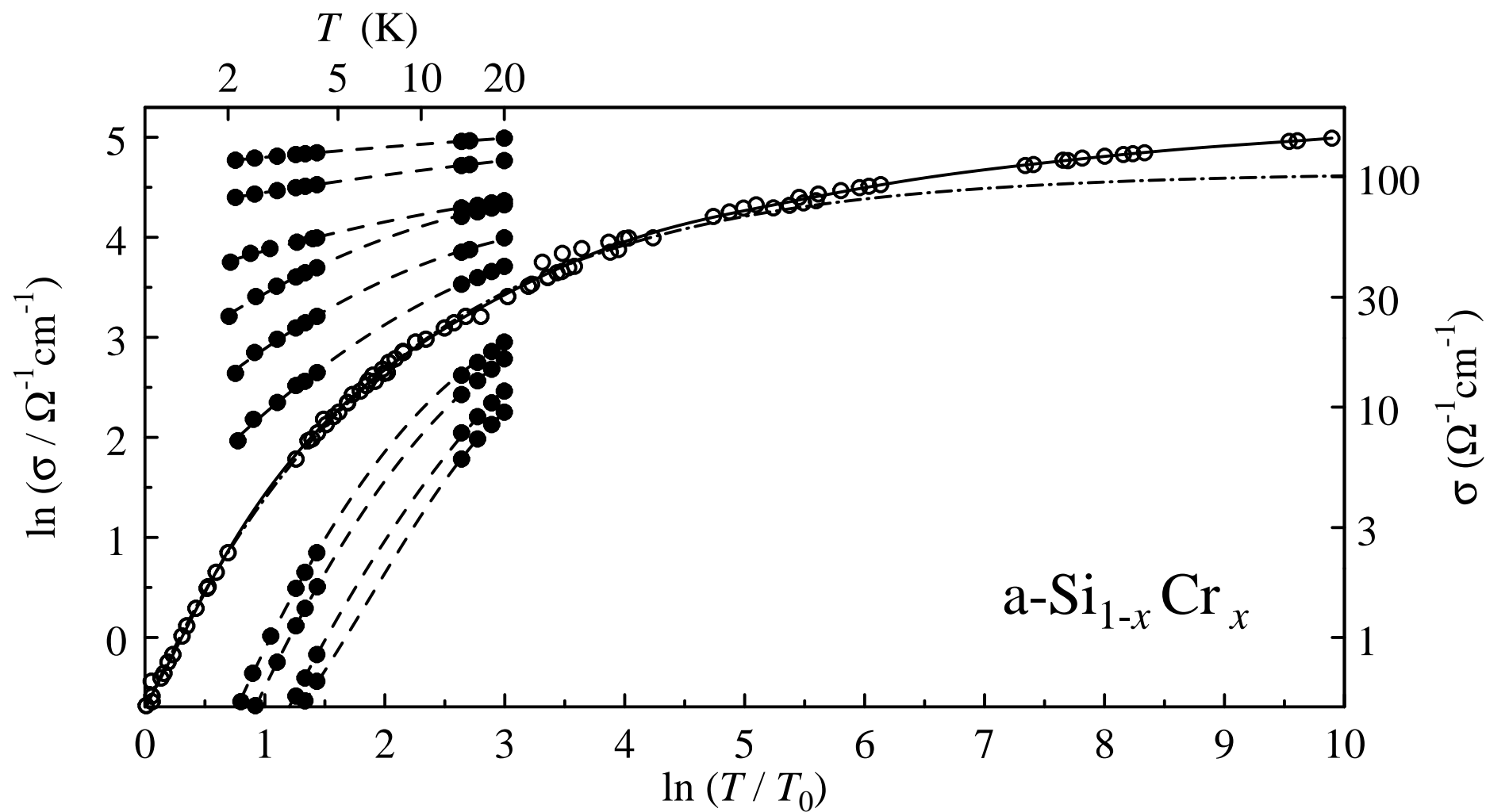Fig. 8

(Mö / Adk)

Fig. 9

(Mö / Adk)

Fig. 10

(Mö / Adk)

Fig. 11 (Mö / Adk)